EVALUATION OF SPECTROGRAMS OF HIGH SPEED STEELS FOR MINOR ELEMENTS. PLATE CALIBRATION METHOD

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ABSTRACT. Minor elements occurring in high speed steels do not exceed a total of two per cent. Such steels of our Works manufacture designated as T.H.S.2 are of the conventional type 18-4-1. The time-scale method of plate calibration due to Smith has been adopted and applied to the ferrous analysis of the above samples; the spectra evaluated and compared with the usual method of log ratio of galvanometer deflections against composition. The elements receiving attention were manganese, silicon and vanadium. Conventional spark technique for exciting spectra was used. The standard deviations of results which have been computed, do not exceed 2 to 3 per cent of contents.

INTRODUCTION

The method of plate calibration for the evaluation of spectrograms can best be carried out in case of alloying elements occurring in small percentages. A method given by Smith (1945) of the British non-ferrous metals Research Association has been used in the analyses of non-ferrous alloys. The method is being adopted and applied to the analysis of ferrous samples such as high speed steels. The elements considered are manganese, silicon and vanadium, the total contents of which do not exceed two per cent in the given alloys.

The basis of method of plate calibration arises out of known relative intensities of manganese triplets 2949.2, 2939.3 and 2933.1. These values were derived from a consideration of "statistical weights" and given by D. M. Smith as 7 : 5 : 3. The ratios are independent of the source of excitation.

As applied to ferrous analysis, it was, however, not possible to include Mn 2949.2 owing to its own interference with an iron line having the same length (Fe II 2949.205). In what follows, therefore, two lines, Mn 2939.3 and Mn 2933.1 formed the calibration pair.

PROCESS

Technique: The apparatus used in exciting the spectra and in the photometric work and the processing of plates is described underneath:

Volts	—	230 A. C.
Condenser	—	0.005 μF
		15,000 V spark
		22,000 V wave peak.

Transformer		1/4 KVA tapping from 15,000 V
Added inductance		Nil
Spark gap	-	2 mm.
Electrodes	-	Samples, chill-cast, flat surface.
Counter electrode	-	H. S. brand carbon also flat surface,
Pre-sparking	-	3 mins.
Spectrograph	-	E 478 Littrow
Sp. phic slit	-	7 divs (=0.0175 mm)
Photometer slit	-	8 divs (=0.016 mm)

The apparatus are all of Hilger's specification and of Hilger manufacture.

Photographic plates	—	Ilford Process
Developer	—	ID 13 No. 1 and 2 in equal proportions.
Development	—	4 mins.

Flat surface technique of spark excitation with a condensed spark of routine type was used.

Reproducibility : In order to test the reproducibility of spectral intensities a continuous spark of 25 secs. duration on a chosen sample against carbon was given with spectra distributed throughout the plate. The data are given in Table I.

TABLE I

	Mn 2939 Deflection	Density D 2939	$D-$Av d)		Mn 2933 Deflection	Density D 2933	$D-$Av (d)	
1	67	0.80	−0.01		120	0.54	0.00	
2	69.5	0.78	−0.03		127.5	0.52	−0.02	
3	66	0.80	−0.01		121	0.54	0.00	
4	65.5	0.81	0.00		120	0.54	0.00	
5	70	0.78	−0.03	$\Sigma d^2=.0100$	126	0.52	−0.02	$\Sigma d^2=.0047$
6	69	0.78	−0.03	Std. deviation	125.5	0.52	−0.02	Std. deviation
7	66	0.80	−0.01		120	0.54	0.00	
8	63	0.82	0.01	$\sigma=\sqrt{\frac{\Sigma d^2}{n}}$	117.5	0.55	0.01	$\sigma=\sqrt{\frac{\Sigma d^2}{n}}$
9	63	0.82	0.01	=0.023	117	0.55	0.01	=0.016
10	66.5	0.80	−0.01	in %	127	0.52	−0.02	in %
11	65	0.81	0.00	2.8%	119.5	0.55	0.01	3%
12	58.5	0.86	0.05		113	0.57	0.03	
13	62.5	0.83	0.02		117.5	0.55	0.01	
14	62.5	0.83	0.02		116.5	0.56	0.02	
15	62	0.83	0.02		117	0.55	0.01	
16	58	0.86	0.05		113.5	0.57	0.03	
17	62	0.83	0.02		116.5	0.56	0.02	
18	63	0.82	0.01		122	0.54	0.00	

Mean 0.81

Mean 0.54
Clear plate Av. 420 mm.

The deflections are the mean of two readings obtained by measuring the line each way as the plate is moved from one side to the other. The standard deviations of densities as obtained was 2.8% for Mn 2939·1 and 3% for Mn 2933·1.

EXPERIMENTAL

A series of three plates A, B and C was used for making the blackening curves. As the distribution of spectra over the plate was of some consequence in sampling, spectra were distributed evenly and were noted. The sequence is shown in Table II

TABLE II

Distribution of spectra

Plate	Alloy used	Exposure	Time of exposure
A.	(13)	1-3	Sec. 10
		4-6	,, 15
		7-9	,, 20
		10-12	,, 30
		13-15	,, 45
		16-18	,, 60
		19,20	,, 90
B & C.	(13)	1-4	,, 10
		5-8	,, 15
		9-12	,, 20
		13-16	,, 25
		17-20	,, 30
		21-24	,, 45
		25-28	,, 60
D.	(13)	1-10	,, 25
		20-29	,, ,,
		11-13	,, 10
		14-16	,, 20
		17-19	,, 30
E.	(13)	1,2,12,13,23,24	,, 10
		3,4,14,15,25,26	,, 20
		5,6,16,17,27,28	,, 30
	(3)	7,18	,, 25
	(4)	8,19	,, ,,
	(7)	9,20	,, ,,
	(30)	10,21	,, ,,
	(42)	11,22	,, ,,
F.	(6)	1-4	,, 25
		13-16	,, ,,
		25-28	,, ,,
	(13)	5,22	,, 10
		6,23	,, 20
		7,24	,, 30
	(3)	8,17	,, 25
	(4)	9,18	,, ,,
	(7)	10,19	,, ,,
	(30)	11,20	,, ,,
	(42)	12,21	,, ,,

The table shows the distribution for all the plates used in the experiment. The spectra are numbered serially from top to bottom.

Spectra with exposure time of 10, 15 etc. to 60 secs. were photographed. The spark used was continuous with pre-sparking as described. The number of spectra of each duration in case of a plate is given in Table II. All such results are included in the table.

BLACKENING CURVES

Blackening curves were drawn from data given in Table III, where mean values of densities and deflections for manganese lines from the three plates A, B and C are given, the density (Sug. Def. Glas., 1946) being defined as

$$D = \log d_0/d$$

where d_0 is the deflection obtained from clear plate, *i.e.*, base plus unexposed processed emulsion and d, deflection due to the line. Such blackening curves are shown plotted in Fig. 1. The plot is of densities against log time of

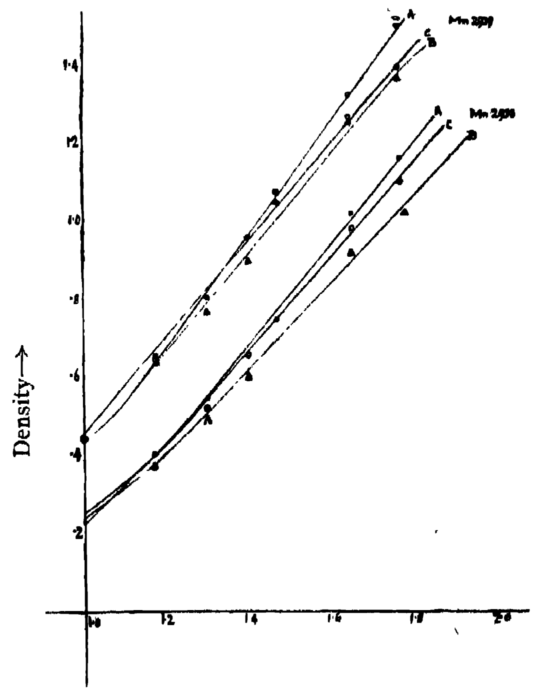


FIG. 1
Blackening curves

exposure. The separation of curves along axes parallel to abscissa are measured giving $\Delta\epsilon$ (log exposure time ratio) for different values of densities.. This is shown in Table III. The mean of log exposure time ratio ($\Delta\epsilon$) thus measured gives, attributing a value 100 to the photographic intensity of Mn 2939, a value equal to 60.3 for Mn 2933; Baly's value on a consideration of statistical weights being 60.1. No correction for background was made but the agreement afforded was excellent.

TABLE III

Time of exposure	I = 100 (Mn 2939) Deflection	I = 100 (Mn 2939) Density	I = 60.3 (Mn 2933) Deflection	I = 60.3 (Mn 2933) Density
10″	A 153	0.44	238	0.23
	B 152.5	0.44	237	0.25
	C 144.4	0.44	222	0.26
	Mean 150	0.44	232.3	0.25
	Log *It*	3.00		2.78
15″	A 89	0.65	159	0.40
	B 79.5	0.63	177	0.37
	C 90.9	0.64	157	0.40
	Mean 86.46	0.64	164.3	0.39
	Log *It*	3.176		2.96
20″	A 62.7	0.80	116.2	0.54
	B 72.4	0.76	137	0.48
	C 67.0	0.75	122	0.51
	Mean 67.3	0.77	125.1	0.51
	Log *It*	3.301		3.081
25″	—	—	—	—
	B 51.2	0.92	103.2	0.61
	C 44.2	0.95	86	0.65
	Mean 47.7	0.94	94.6	0.63
	Log *It*	3.398		3.178
30″	A 36	1.04	73	0.74
	B 35.5	1.07	74.5	0.75
	C 34.1	1.07	66	0.78
	Mean 35.2	1.06	71.2	0.76
	Log *It*	3.477		3.257
45″	A 19	1.32	39	1.01
	B 24	1.25	51	0.91
	C 22	1.26	42.4	0.97
	Mean 21.7	1.28	44.1	0.96
	Log *It*	3.653		3.433
60″	A 12.5	1.50	28	1.15
	B 18.2	1.36	41.2	1.01
	C 16.0	1.39	32.5	1.09
	Mean 15.6	1.42	33.9	1.08
	Log *It*	3.778		3.558

D (Density)	Plate A	Plate B	Plate C
0.5	—	2.58	2.25
0.6	2.40	2.50	2.20
0.7	2.25	2.40	2.25
0.8	2.20	2.35	2.20
0.9	2.10	2.35	2.20
1.0	2.10	2.30	2.20
1.1	2.15	—	2.15
1.2	2.18	—	
$\Delta\epsilon$	0.22	0.24	0.22

Mean $\Delta\epsilon$ 0.22
Antilog 0.78

Photographic Intensity

Mn 2229 100
Mn 2933 60.3

Data according to Baly
Mn 2939 100
Mn 2933 60.1

Clear plate Av. 406 mm.

In all subsequent experiments a calibration pattern as described above was included in the plate. Blackening curves were drawn in each case. Data for D, E and F plates are given in Table IV-VI.

TABLE IV

Time of exposure	Mn 2939		Mn 2933		Density	Plate D
	Deflection	Density	Deflection	Density		
10″	128	0.42	193	0.24	0.5	2.20
	124	0.44	192	0.25		
	114	0.47	186.5	0.26	0.6	2.45
Mean	123	0.44	190.5	0.25	0.7	2.70
20″	53	0.54	98.5	0.54		
	53	0.53	99.5	0.53	Mean	2.45
	54	0.52	102	0.52	Δε	0.245
					Antilog	0.755
Mean	53.3	0.53	100	0.53	Photographic Intensity	
30″	32	1.03	64.5	0.72		
	36	0.97	72	0.67		
	34.5	0.99	70	0.68	Mn 2939	100
Mean	34.2	1.00	68.8	0.69	Mn2933	56.9

Clear plate Av. 338 mm

TABLE V

Time of exposure	Mn 2939		Mn 2933		Density	Plate E
	Deflection	Density	Deflection	Density		
10″	177.5	0.35	251	0.20	0.4	2.55
	183.0	0.34	261.5	0.19		
	171.5	0.37	251.5	0.20	0.5	2.32
Mean	177.3	0.35	255.0	0.20	0.6	2.15
20″	117.5	0.53	190	0.32	0.7	2.20
	91.5	0.64	159.7	0.40	Mean	2.28
	81.2	0.69	149	0.43	Δε	0.228
Mean	96.7	0.62	166.2	0.38	Antilog	0.772
30″	57.7	0.84	110.2	0.56	Photographic Intensity	
	59.0	0.83	112.7	0.55		
	52.5	0.88	103.2	0.59	Mn 2939	100
Mean	56.4	0.85	108.7	0.57	Mn 2933	59.2

Clear plate Av. 400 mm.

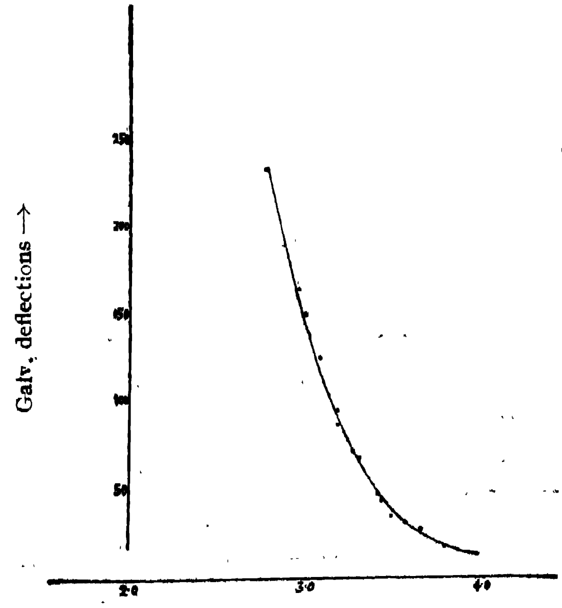
TABLE VI

Time of Exposure	Mn 2939 Deflection (Mean)	Mn 2939 Density (Mean)	Mn 3939 Deflection (Mean)	Mn 3939 Density (Mean)	Density	Plate F.
10″	172.8	0.36	258.7	0.44	0.4	2.40
20″	81.7	0.69	152.7	0.42	0.5	2.13
30″	48	0.92	100.2	0.60	0.6	2.00
					0.7	2.00
					0.8	2.03
					Mean	2.11
					$\Delta\epsilon$	0.211
					Antilog	0.789
					Photographic Intensity	
					Mn 2939	100
					Mn 2933	61.5

Clear plate Av. 400 mm.

Giving the photographic intensity a value 100 for Mn 2939, the values were 56.9, 59.2 and 61.5 respectively for Mn 2933 for plates D, E and F.

Having constructed the blackening curves for plates A, B and C (Fig. 1) and obtained the mean $\Delta\epsilon$, a second plot was made with log It as one axis and deflection the other. This shows little scatter. The data are taken out of Table III. The calibration curve so obtained is shown in Fig. 2.



Log It

FIG. 2

Calibration curve

We now come to a stage of drawing intensity-calibration curves. As in all cases of high speed steel analysis exposures having been standardised at a fixed value of 25 secs., a parameter log I_{25} derived from log It-log 25 was used instead of log It in plotting intensity-calibration curves. Such a curve is shown plotted in Fig. 3, for plate D. The data are from Table VII.

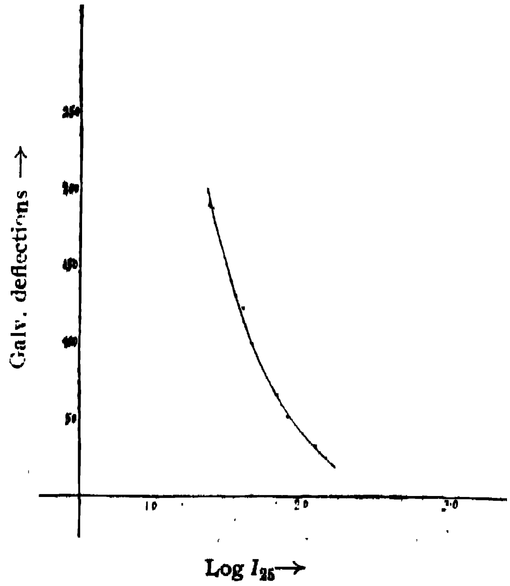


FIG. 3
Intensity calibration curve

TABLE VII

Time of exposure	Mn 2939		Mn 2933	
	Deflections	Log I_{25} (log It-log 25)	Deflections	Log I_{25} (log It-log 25)
Plate D. 10″	123	1.602	190.5	1.357
20″	53.3	1.903	100	1.658
30″	34.2	2.079	68.8	1.834
Clear plate Av. 338 mm.				
Plate E. 10″	177.3	1.602	255	1.374
20″	96.7	1.903	166.2	1.675
30″	56.4	2.079	108.7	1.851
Clear plate Av. 400 mm.				
Plate F. 10″	172.8	1.602	258.7	1.391
20″	81.7	1.903	152.7	1.692
30″	48.0	2.079	100.2	1.868
Clear plate Av. 400 mm.				

Verification of results.—

Suggestion arising out of Smith's paper for verification of variation with time of the intensity of emission was tried. No systematic variation was evident and no generalisation was possible as with Smiths. The result for plate D is tabulated in Table VIII.

TABLE VIII

Plate D

Exp. No.	Mn 2939		Mn 2933		Exp. No.	Mn 2939		Mn 2933	
	log I_{25}	I_{25}	log I_{25}	I_{25}		log I_{25}	I_{25}	log I_{25}	I_{25}
1	1.93	85.1	1.68	47.9	20	2.00	100.0	1.73	53.7
2	1.90	79.4	1.63	42.7	21	1.98	95.5	1.72	52.5
3	1.92	83.2	1.66	45.7	22	1.99	97.7	1.72	52.5
4	1.99	97.7	1.72	52.5	23	1.98	95.5	1.72	52.5
5	1.96	91.2	1.71	51.3	24	2.02	104.7	1.74	55.0
6	2.01	102.3	1.75	56.2	25	1.98	95.5	1.70	50.1
7	1.99	97.7	1.71	51.3	26	1.93	85.1	1.65	44.7
8	1.99	97.7	1.71	51.3	27	1.93	85.1	1.63	42.7
9	1.96	91.2	1.70	50.1	28	1.94	87.1	1.66	45.7
10	1.98	95.5	1.71	51.3	29	1.93	85.1	1.64	43.7

Av. on 100% basis.

100 : 53.6

In a following table is shown the results of chemical analysis and the uses to which the alloys are put. Useful line pairs (Harrison, 1939) for purposes of calibration and for analysis and internal standards are shown in Tables IX and X.

TABLE IX

Chemical analysis

Sample No.	Use	Mn	Si	V	Cr	W
(3)	Standard	0.22	0.17	1.17	4.27	18.64
(4)	Standard	0.20	0.22	1.22	4.42	18.84
(6)	Test alloy	0.21	0.16	1.22	4.35	19.05
(7)	Standard	0.20	0.14	1.26	4.40	19.83
(13)	Calibration	0.24	0.20	1.44	4.70	20.79
(30)	Standard	0.30	0.16	1.33	4.27	17.98
(42)	Standard	0.25	0.23	1.40	3.60	19.39

TABLE X

Line pairs

Calibration	Mn 2939.30	Mn 2933.06
Analysis	Mn 2933.06 Si I 2881 58 VII 3062.70	
Internal Standard	Fe I 2936.90 Fe II 2885.93 Fe II 3062.23	

Calibration curves.—

Two series of plates E and F are taken to include calibration patterns distributed evenly over the plate as also exposures from standards. Plate E includes exposures from a test alloy. Results from plates E and F are shown in Tables XI and XII. The results include the usual log R, ratio.

TABLE XI

Plate E

Mn Chart

Sample No.	Mn 2933 deflection	Fe 2937 Deflection	$R=\frac{Mn}{Fe}$	log R	log I_{Mn}	log I_{Fe}	log ratio of Ints. (+)
(3)	115.7	39.5	2.92	0.465	1.81	2.15	0.34
(4)	115.0	36.0	3.19	0.504	1 82	2.18	0.36
(7)	115.0	35 5	3.24	0.511	1.82	2.18	0.36
(30)	80.0	37.0	2.16	0.335	1.96	2 17	0.21
(42)	83.0	37.7	2.20	0.342	1.95	2.16	0.21

V Chart

Sample No	V3063 Deflection	Fe 3062 Deflection	$R=\frac{V}{Fe}$	log R	log I_V	log I_{Fe}	log ratio of Ints. (+)
(3)	66.7	35.5	1 88	0 27	2 03	2.18	0 15
(4)	49.2	29.7*	1.66	0.22	2.11	2.21	0.10
(7)	42.7	27.7	1 54	0 18	2.14	2.22	0.08
(30)	48.7	28 2	1.73	0.24	2.11	2.21	0.10
(42)	42.5	29	1.46	0.16	2.14	2.21	0.07

TABLE XI (*contd.*)

Si Chart

Sample No.	Si 2881 Deflection	Fe 2886 Deflection	$R = \frac{Si}{Fe}$	log R	log I_{Si}	log I_{Fe}	log ratio of intensities (+)
(3)	187	150	1.25	0.097	1.56	1.68	0.12
(4)	158.5	135.5	1.19	0.075	1.65	1.74	0.09
(7)	162.2	132.5	1.22	0.086	1.64	1.75	0.11
(30)	142.7	136.5	1.04	0.017	1.71	1.73	0.02
(42)	131.5	133.7	0.98	0.01	1.75	1.74	−0.01

TABLE XII

Plate F

Mn Chart

Sample No.	Mn 2933 Deflection	Fe 2937 Deflection	$R = \frac{Mn}{Fe}$	log R	log I_{Mn}	log I_{Fe}	log ratio of intensities (+)
(3)	109.2	42.5	2.57	0.41	1.82	2.11	0.29
(4)	112.5	36.75	3.07	0.49	1.80	2.14	0.34
(7)	123.2	41.5	2.97	0.47	1.77	2.11	0.34
(30)	85.7	46.2	1.85	0.27	1.91	2.09	0.18
(42)	79.2	42.5	1.86	0.27	1.94	2.10	0.16

V Chart

Sample No.	V 3063 Deflection	Fe 3062 Deflection	$R = \frac{V}{Fe}$	log R	log I_V	log I_{Fe}	log ratio of intensities (+)
(3)	62	34.2	1.81	0.26	2.01	2.15	0.14
(4)	50.2	31.5	1.595	0.20	2.08	2.17	0.09
(7)	55.2	35.7	1.55	0.19	2.05	2.14	0.09
(30)	49.2	34.0	1.45	0.16	2.08	2.15	0.07
(42)	37.5	26.7	1.405	0.15	2.13	2.20	0.07

TABLE XII (*contd.*)

Si Chart

Sample No.	Si 2881 Deflection	Fe 2886 Deflection	$R=\frac{\text{Si}}{\text{Fe}}$	log R	log I_{Si}	log I_{Fe}	log Ratio of intensities (+)
(3)	169.5	130.5	1.30	0.11	1 63	1 74	0.11
(4)	145 0	120.7	1.20	0.08	1.69	1.78	0.09
(7)	152.7	130	1.17	0 07	1 67	1.74	0.07
(30)	132.2	136.2	0 971	0.01	1.73	1.72	0.01
(42)	123 0	122.5	1.003	0.00	1.77	1.77	0.00

deflection due to analysis line to that due to internal standard and log $I_{2.5}$ values and their differences derived from appropriate calibration curves E and F (not shown) for elements manganese, silicon and vanadium. Calibration curves were plotted with log R and log ratio of intensities against composition. Such curves for elements manganese, silicon and vanadium are shown plotted in Fig. 4. Discussion of results follows. Plate F includes a test alloy. From the appropriate intensity calibration curve (F), compositions of Mn, Si, and V were derived. Values are tabulated in Tables XIII, XIV and XV).

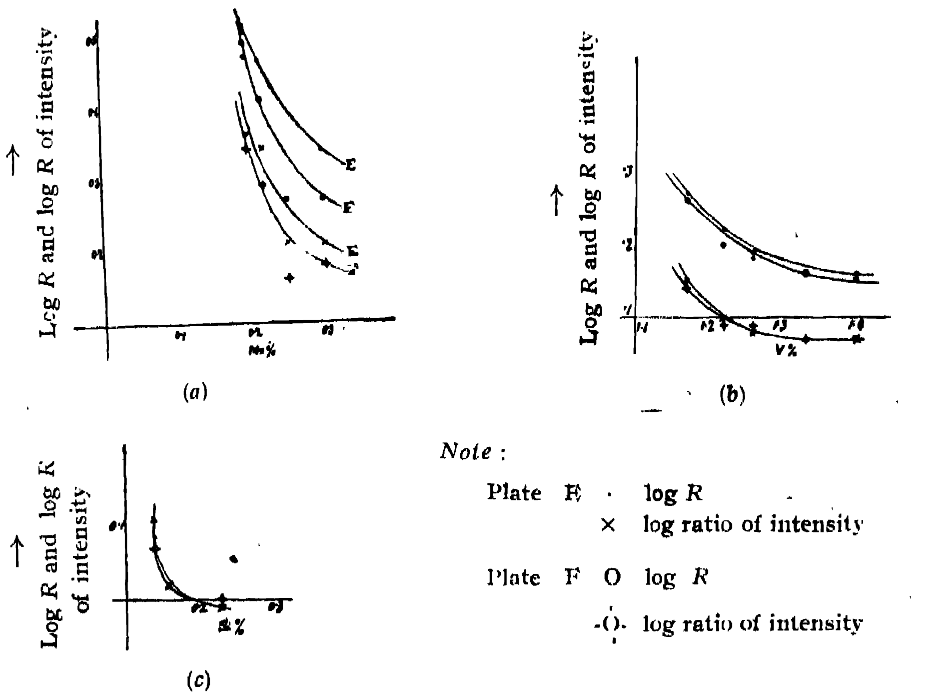


FIG. 4

TABLE XIII

Readings for Sample (6)

Mn

(0.21)

	Fe I 2937 Deflection	Mn 2933 Deflection	$R=\frac{Mn}{Fe\ I}$	log R	% (Calculated)	$I_{Fe\ I}$	Mn	log ratio of Ints.	% Calculated (b)	Diff. b Av$_b$ (d)	Sq. of Diffs. $\times 10^{-6}$
1	41.5	178.5	3.10	0.49	0.200	2.11	1.75	0.36	0.198	−0.004	16
2	40	122	3.05	0.48	0.200	2.12	1.77	0.35	0.200	−0.002	4
3	46.5	128.5	2.76	0.44	0.210	2.09	1.75	0.34	0.202	0.000	—
4	38	120	3.16	0.50	0.197	2.13	1.78	0.35	0.200	−0.002	4
13	45	128.5	2.86	0.46	0.205	2.10	1.75	0.35	0.200	−0.002	4
14	45.5	128	2.81	0.45	0.208	2.09	1.75	0.34	0.202	0.000	—
15	38.5	114.5	2.98	0.47	0.202	2.13	1.79	0.34	0.202	0.000	—
16	35	112	3.20	0.50	0.197	2.15	1.81	0.34	0.202	0.000	—
25	40	115	2.87	0.46	0.205	2.12	1.79	0.33	0.206	0.004	16
26	48.5	126	2.60	0.42	0.214	2.08	1.76	0.32	0.208	0.006	36
27	41.5	126.5	3.05	0.48	0.200	2.11	1.75	0.36	0.198	−0.004	16
28	52.5	135	2.57	0.41	0.218	2.06	1.73	0.33	0.206	0.004	16
					Σ2.456 Mean 0.205				Σ2.424 Mean 0.202		Σ112

Standard deviation. $\sigma=\sqrt{\frac{\Sigma d^2}{n}}=1.5\%$ of content.

TABLE XIV

Readings for Sample (6)
Si
(0.16)

Exp. No.	Fe II 2886 Deflection	Si I 2881 (Deflection)	$R=\frac{\text{Si I}}{\text{Fe II}}$	log R	% (Calculated)	$I_{\text{Fe II}}$	$I_{\text{Si I}}$	log ratio of Ints.	% (Calculated) b	Diff. b-Av. (d)	Sq of Diffs. $\times 10^{-6}$
1	126	150	1.19	0.08	0.139	1.75	1.68	0.07	0.140	−0.001	1
2	118	144.5	1.22	0.09	0.137	1.78	1.70	0.08	0.140	−0.001	1
3	119	149.5	1.255	0.10	0.136	1.78	1.68	0.10	0.140	−0.001	1
4	125	154	1.23	0.09	0.137	1.76	1.67	0.09	0.140	−0.001	1
13	131	157.5	1.20	0.08	0.139	1.74	1.66	0.08	0.140	−0.001	1
14	123.5	150.5	1.22	0.09	0.137	1.76	1.68	0.08	0.140	−0.001	1
15	118.5	149	1.26	0.10	0.136	1.78	1.68	0.10	0.140	−0.001	1
16	112.5	143.5	1.275	0.11	0.135	1.80	1.70	0.10	0.140	−0.001	1
25	134.5	159	1.18	0.07	0.140	1.73	1.66	0.07	0.140	−0.001	1
26	148	168	1.14	0.06	0.141	1.69	1.64	0.05	0.142	0.001	1
27	156.5	173.5	1.11	0.05	0.142	1.66	1.62	0.04	0.144	0.003	9
28	161.5	184	1.14	0.06	0.141	1.65	1.60	0.05	0.142	0.001	1
					Σ 1.660 Mean 0.138				Σ 1.688 Mean 0.141		Σ20

Standard deviation $\sigma=\sqrt{\frac{\Sigma n^2}{n}} < 1\%$ of content.

TABLE XV

Readings for Sample (6)

V

(1.22)

Exp. No.	VII 3063 (Deflection)	Fe II 3062 Deflection	$R = \frac{\text{VII}}{\text{Fe II}}$	log R	% Calculated	I VII	I Fe II	log ratio of Ints.	% Calculated (b)	Diff. b-Av. (d)	Sq. of Diffs. $\times 10^{-6}$
1	75	50	1.50	0.18	1.271	1.96	2.07	0.11	1.203	−0.014	196
2	55	36	1.53	0.18	1.271	2.05	2.14	0.09	1.242	0.025	625
3	51	30	1.70	0.23	1.200	2.07	2.18	0.11	1.203	−0.014	196
4	50	29	1.72	0.24	1.190	2.07	2.18	0.11	1.203	−0.014	196
13	50	30.5	1.64	0.21	1.220	2.07	2.17	0.10	1.220	0.003	9
14	57	34.5	1.65	0.22	1.210	2.04	2.15	0.11	1.203	−0.014	196
15	48.5	32	1.515	0.18	1.271	2.08	2.16	0.08	1.280	0.063	3969
16	46.5	27	1.725	0.24	1.190	2.09	2.19	0.10	1.220	0.003	9
25	52	30.5	1.70	0.23	1.200	2.06	2.17	0.11	1.203	−0.014	196
26	52.5	33	1.59	0.20	1.238	2.06	2.16	0.10	1.220	0.003	9
27	58	34	1.70	0.23	1.200	2.04	2.15	0.11	1.203	−0.014	196
28	59	36	1.56	0.19	1.254	2.03	2.14	0.11	1.203	−0.014	196
					Σ 14.715 Mean 1.226				Σ 14.603 Mean 1.217		Σ 4993

Standard deviation $\sigma = \sqrt{\frac{\Sigma d^2}{n}}$ = 1.5% of content.

The standard deviations of 12 results are :

1.5 for Mn
$<$ 1.0 for Si
1.5 for V.

The accuracy obtained is comparable to usual log R method.

DISCUSSION OF RESULTS.

In the calibration curves given by the two methods (Fig. 4) accuracy obtained was nearly constant. Calibration did not usually produce a single curve applicable to the two plates. This is the more remarkable in the case of manganese. For silicon, however, a single curve suffices. For vanadium two curves are given form sets of closely lying parallel curves.

On the application of background correction it can be said that no standard critique of spectral background evaluation exists; the emphasis is laid on having a clean plate with little background. Background calculation adds materially to time, a fact which militates against ordinary routine business. No attempt was thus made to calculate this factor. These facts point to a conclusion that plate calibration does not usually compensate for responses of plates. Nonetheless, the method described is simple and can be of general use. Further work might also give better corroborative results.

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